PREPARATION AND IMMOBILIZATION OF PALLADIUM(II) AND NICKEL(II) SALEN COMPLEXES ONTO MCM-41 FROM RICE HUSK FOR SUZUKI-MIYAURA AND OXIDATION REACTIONS

SALIH HAMZA ABBAS

UNIVERSITI SAINS MALAYSIA

2015

PREPARATION AND IMMOBILIZATION OF PALLADIUM(II) AND NICKEL(II) SALEN COMPLEXES ONTO MCM-41 FROM RICE HUSK FOR SUZUKI-MIYAURA AND OXIDATION REACTIONS

by

SALIH HAMZA ABBAS

Thesis submitted in fulfillment of the requirement for the degree of

Doctor of Philosophy

August 2015

DEDICATIONS

This thesis is dedicated to

My parents. May Allah forgive them

and

My family

ACKNOWLEDGEMENT

In the Name of Allah, Most Gracious, Most Merciful

Praise is due to Allah Whose worth cannot be described by speakers.

I am pleased to place on record my special gratitude and thanks to the government of Iraq, the government of Malaysia, University of Basrah and University Science Malaysia for the financial and technical supports.

My sincere thanks go to my supervisor, Professor Farook Adam for his guidance, insightful comments and constant support during the experimental part and in the writing of the thesis.

I would like to thank the staff members of Institute of Postgraduate Studies (IPS), School of Chemical Sciencess, School of Physics and School of Biological Sciences, USM for their help in the use of the necessary equipments and analysis.

I would like to give special thanks to my past and present labmates and my friends for their help, the knowledge sharing and instilling confidence.

Last but not least, my heartfelt gratitude towards my family: particularly my sisters, my brother, my loving wife and my kids for their continuous love, prayer, support and patience throughout my PhD study. Thank you all so much.

TABLE OF CONTENTS

Page

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SCHEMES

Page

LIST OF SYMBOLS

A	Frequency factor
a_o	Hexagonal unit cell parameter
C_o	Initial concentration
C_t	Concentration at time
cm^{-1}	Wavenumber
d_{100}	Diffraction plane at 100
E_a	Activation energy
g	Gram
h	Hour
Hz	Hertz
K	Kelvin
k	Kilo, (1000)
k_a	Apparent rate constant
kcal	Kilocalorie
kHz	Kilo Hertz
kv	Kilo volt
L	Litter
ln	Natural logarithm
log	Logarithm
M	Molarity
mA	Milli amper
min	minute
mL	Milliliter

mm	Millimeter
mm Hg	millimeter of mercury
mmol	Millimole
mol	Mole
nm	Nanometer
^{o}	Degree
^{o}C	Degree Celsius (degree centigrade)
P/P_o	Relative Pressure
Q^2	Silicon atom bearing two hydroxyl groups and bonded to two silicon atoms via oxygen bond
Q^3	Silicon atom bearing one hydroxyl groups and bonded to three silicon atoms via oxygen bond
Q^4	Silicon atom not bonded to any hydroxyl group and bonded to four other silicon atoms via oxygen bond
R	Gas constant
T	Absolute temperature
T	Tesla (unit for measuring magnetic induction)
t	Time
V_p	Pore volume
W_d	Pore diameter
X	Halogen
x	Unreacted concentration
μL	Microliter
λ	Wavelenght
δ	Chemical shift

θ_m	magic angle-spinning
%	Percentage
%T	Percentage Transmitance
√	The square root

LIST OF ABBREVIATIONS

a	Primary concentration
APTES	3-aminopropyltriethoxysilane
BET	Brunauer, Elmmet and Teller method
BJH	Barrett, Joyner and Halenda method
ca.	Calculated
cm^3/g	Cubic meter per gram
^{13}C NMR	Carbon-13 Nuclear Magnetic Resonance
CPTES	3-(chloropropyl)triethoxysilane
CTAB	Cetyltrimethylammonium bromide
CuKα	X-ray spectral line for copper bombarded with energy sufficient to give intense X-ray emission
d	Doublet
d_6	Deuterated solvent
DMF	Dimethylformamide
DCM	Dichloromethane
DMSO	Dimethyl sulfoxide
EDX	Energy Dispersive X–ray
Et_3N	Triethylamine
etc.	et cetera
FAO	Food and Agriculture Organization of the United Nations
FID	Flame ionization detector
FT-IR	Fourier Transmitance Infrared Spectroscopy

GC	Gas Chromatography
GC-MS	Gas Chromatography Mass Spectroscopy
H4	Hysteresis loop type 4
^{1}H NMR	Hydrogen-1 Nuclear Magnetic Resonance
IUPAC	The International Union of Pure and Applied Chemistry
M41S	Mesoporous silicas
m^2/g	Square meter per gram
MAS NMR	Magic angle–spinning Nuclear Magnetic Resonance
MCM-41	Mobil Crystalline Material Number 41
PAG	Polyethylene glycol
pg	page
pH	The Hydrogen Function
PMOs	Periodic measoporous organoslicas
ppm	Part per Million
R	Alkyl group
RH	Rice husk
RHA	Rice husk ash
RMM	Rice Market Monitor
Rt	Retention time
r.t.	Room temperature
s	singlet
salen	Salicyladimine
SBA-15	Santa Barbara Amorphous Material Number 15
SDAs	Structure-directing agents
SEM	Scanning Electron Microscopy

^{29}Si NMR	Sillicon-29 Nuclear Magnetic Resonance
t	Triplet
TEM	TEM Transmission Electron Microscopy
TEOS	Tetraethyl orthosilicate
TMOS	Tetramethyl orthosilicate
t-BuOOH	tert-butyl hydroperoxide
$^{v}/_{v}$	Volume/ volume
XRD	Powder X–ray Diffraction

PENYEDIAAN DAN SEKATGERAK KOMPLEKS SALEN PALADIUM(II) DAN NIKEL(II) KE ATAS MCM-41 DARIPADA SEKAM PADI UNTUK TINDAK BALAS SUZUKI-MIYAURA DAN TINDAK BALAS PENGOKSIDAAN

ABSTRAK

MCM-41 daripada abu sekam padi (RHA) telah berjaya disintesis dangan menggunakan cetiltrimetilammonium bromida sebagai agen pegasal melalui kaedah sol-gel pada sahu 100 ^{o}C. MCM-41 telah difungsikan dengan 3-kloropropiltrietoksisilana (CPTES) sebagai agen pencantuman dan pepejal yang diperoleh dilabel sebagai Cl-MCM-41. Ini diikuti dengan dua kali immobilisasi kompleks *N,N'*-bis (4-hidroksisalisilidina)etilenadiimina-paladium(II) dan *N,N'*-bis (4-hidroksisalisilidina)etilenadiimina-nikel(II) melalui dua kumpulan hidroksil pada Cl-MCM-41. Dua mangkin heterogen ini telah diperoleh dan dilabel sebagai MCMSalenPd dan MCMSalenNi. Pencirian kedua-dua mangkin dan immobilisasinya telah buktikan dengan menggunakan spektrometer infra merah (FT-IR), Pembelauan Sinar-X (XRD), penyerapan N_2, mikroskop transmisi elektron (TEM), mikroskop elektron imbasan (SEM), resonan nuklear magnet C-13 (^{13}C MAS NMR), resonan nuklear magnet Si-29 (^{29}Si MAS NMR), tenaga serakan sinar-X (EDX) dan spektroskop serapan atom (AAS). Mangkin MCMSalenPd telah digunapakai untuk tindak balas Suzuki-Miyaura antara bromobenzena dengan asid fenilboronik. Mangkin ini sangat stabil dan memberikan aktiviti yang berkesan dalam masa 2 jam pada 130 ^{o}C. Peratusan penukaran adalah 98.7% dengan 100% kepilihan. Kajian kinetik menunjukkan tindak balas mematuhi hukun kadar pseudo-pertama. Tenaga pengaktifan adalah 0.393 kcal mol^{-1}. Mangkin ini telah diguna semula lebih daripada lima kali tanpa menjejaskan aktiviti pemangkin. Mangkin MCMSalenNi telah digunakan untuk tindak balas pengoksidaan benzil alkohol

dengan asid periodik sebagai agen pengoksidaan. Mangkin ini sangat stabil dan menunjukkan aktiviti pemangkinan yang berkesan. Peratusan penukaran adalah 98.4% dengan 48.8% kepilihan apabila tindak balas dilakukan untuk 1.5 jam pada suhu 90 ^{o}C. Kajian kinetik menunjukkan hukum kadar pseudo-pertama dan tenaga pengaktifan adalah 0.0538 kcal mol^{-1}. Mangkin ini boleh digunakan lebih daripada enam kali.

PREPARATION AND IMMOBILIZATION OF PALLADIUM(II) AND NICKEL(II) SALEN COMPLEXES ONTO MCM-41 FROM RICE HUSK FOR SUZUKI-MIYAURA AND OXIDATION REACTIONS

ABSTRACT

MCM-41 was successfully prepared from rice husk ash (RHA) using cetyltrimethylammonium bromide as a directing agent via sol-gel method at 100 ^{o}C. MCM-41 was functionalized with 3-chloropropyltriethoxysilane (CPTES) as a functioning agent and the solid obtained was labeled as Cl-MCM-41. This was followed by double immobilization of *N,N′*-bis(4-hydroxysalicylidene)ethylenediimine palladium(II) and *N,N′*-bis(4-hydroxysalicylidene)ethylenediimine nickel(II) complexes via their two hydroxyl groups onto Cl-MCM-41. Two new heterogeneous catalysts were obtained and designated as MCMSalenPd and MCMSalenNi. The two prepared catalysts were fully characterized and the double immobilization of the two complexes was confirmed using fourier transform infrared (FT-IR), X-ray diffraction (XRD), N_2 sorption measurements, transmission electron microscopy (TEM), scanning electron microscopy (SEM), solid state C-13 nuclear magnetic resonance (^{13}C MAS NMR), solid state Si-29 nuclear magnetic resonance (^{29}Si MAS NMR), energy dispersive X-ray elemental analysis (EDX) and atomic absorption spectroscopy (AAS). The MCMSalenPd catalyst was examined for Suzuki-Miyaura C-C coupling reaction of bromobenzene with phenylboronic acid. The catalyst had good stability and excellent activity within 2 hour at 130 ^{o}C. The conversion percentage was 98.7% with 100% selectivity. The kinetic studies showed the reaction followed a pseudo first order rate law. The activation energy was determined to be about 0.393 kcal mol^{-1}. The catalyst was reused for more than five catalytic cycles without significant loss of activity. The MCMSalenNi catalyst was examined for the oxidation reaction of benzyl

alcohol using periodic acid as oxidant. The catalyst was found to have good stability and excellent activity. The conversion percentage was 98.4% with 48.8% selectivity when the reaction was carried out for 1.5 hour at 90 ^{o}C. The kinetic study showed a pseudo first order rate law and the activation energy was determined to be about 0.0538 kcal mol^{-1}. The catalyst was reused for more than six catalytic cycles with good reusability.

CHAPTER 1

INTRODUCTION

1.1 General entrance

Catalysis is the increase in the rate of a chemical reaction due to the partnership of a substance called a catalyst. Catalysts have become an even more important area of chemical research since metals started to be used in 1796 by Von Marum for dehydrogenation of alcohols. The term “catalyst” was introduced as early as 1836 by John Jacob Berzelius when he supposed that catalysts had special abilities that could cause the convergence of chemical substances. Catalysis can be divided into two types: homogeneous catalysis, in which either a gas (or a liquid) phase was engaged in both as the catalyst and the reactant and heterogeneous catalysis, in which the catalysts and the reactant are in different phases (Satterfield, 1991); solid catalysts are used generally with liquids or gaseous reactants.

Broadly speaking, there are three main functions for a substance which acts as a catalyst; activity, selectivity and stability. The preference between them depends on the specific demands in a certain chemical process (Hagen, 2006).

The term “catalyst activity” refers to the rate of one or more reactions continuing to chemical equilibrium in the presence of the catalyst. It depends on many variable parameters, like pressure, temperature, the mole ratio of reactants and products and the catalyst quantity. The term “catalyst selectivity” means the extent to which the catalyst expedites the reaction to shape one or more of the coveted products. The term “catalyst stability” means its active time in the industrial process; it depends on several factors, like decomposition, cocking and poisoning. The

catalyst damping can be tracked by detecting either its activity or selectivity as a function of time.

Furthermore, the important considerations which are most concerned about in the designing of catalysts are that they be economically useful and friendly towards the environment in their industrial applications. Many of these qualities can be found in heterogeneous catalyst systems mainly due to their inherent properties; the heterogeneous catalyst can be recovered easily by a simple filtration process so the coveted product will be un-contaminated by transition metals or complexes though some leaching which may occur. In addition, the catalyst usually can be reused in subsequent reactions. In industrial use, both types of catalysts have advantages and disadvantages, which are briefly compared in Table 1.1 (Hagen, 2006).

1.2 Heterogenization of homogeneous catalysts

To implement the separation and reusability of the homogeneous catalysts, lots of approaches have been evolved to immobilize the homogeneous catalysts to achieve heterogenization. The immobilization of the homogeneous catalyst can be accomplished by supporting the homogeneous catalyst molecules by different ways involving suitable inorganic, organic and so called hybrid materials. For example, this can take place on inorganic support like silica, clay, zeolites and heteropoly acids (Kuźniarska-Biernacka et al., 2011; Uruş et al., 2013; Yu et al., 2013) and for organic support like carbon, dendrimers, polymeric ligands and and polyelectrolytes (Chang et al., 2008; Deraedt et al., 2014; Wang et al., 2012). The theme of immobilization has been a subject of diverse publications and several prior reviews

(Selvam et al., 2012; Wight and Davis, 2002). In this way many homogeneous catalysts have been immobilized on different supports in order to get a better understanding of this strategy in recent years (Steiner et al., 2004).

Table 1.1: Comparison of homogeneous and heterogeneous catalysts (Hagen, 2006).

	Homogeneous	Heterogeneous
Effectivity		
Active centers	All metal atoms	Only surface atoms
Concentration	Low	High
Selectivity	High	Lower
Diffusion problems	Practically absent	Present
Reaction conditions	Mild (50–200 ^{o}C)	Severe (often >250 ^{o}C)
Applicability	Limited	Wide
Activity loss	Cluster formation; poisoning	Crystallites; poisoning
Catalyst properties		
Structure/stoichiometry	Defined	Undefined
Modification possibilities	High	Low
Thermal stability	Low	High
Catalyst separation	Often laborious: chemical decomp., distillation, extraction	Fixed-bed: unnecessary Suspension: filtration
Catalyst recycling	Possible	Fixed-bed: unnecessary Suspension: easy
Cost of catalyst losses	High	Low

1.3 Silica as support material

1.3.1 Silica abundance

A lot of homogeneous catalytic systems have been successfully immobilized in relation to diverse silica supports. The silica and oxygen are the most abundant components in the earth's crust, with about 55% $^{w}/_{w}$ of the earth's surface and its existence either as silicate $SiO_3^{=}$ or as silica with anhydrous formula SiO_2 or with hydrated formula $SiO_2.xH_2O$ (Scott, 1993). The silica also exists in mineral ores like quartz and granite and in cereal plants like rice and barley (Unger, 1979).

1.3.2 Surface nature of silica

Studies on silica started in the 1930s and led to the understanding of the nature of the silica surface (Zhuravlev, 2000). Due to the considerable spectral and chemical data, it has become clear that silica has two different functional groups, i.e. the siloxane (≡Si–O–Si≡) in the bulk and numerous forms of silanol groups (≡Si–OH) on the surface.

According to Nuclear Magnetic Resonance (NMR) studies, there are three types of siloxane groups (≡Si–O–Si≡) which can be represented by the following representation $Q^n = Si(OSi)_n(OH)_{4-n}$, where n = 2–4 which refers to the number of bridging bonds (–O–Si) bonded to the central Si atom, i.e. Q^2, two siloxane bonds to the central silicon atom, Q^3, three siloxane bonds to the central silicon atom and Q^4, four siloxane bonds to the central silicon atom as shown in Figure 1.1. Moreover, experimentally there are two types of silanol groups found on the surface of silica: the isolated group (a single hydroxyl group bonds to the silicon atom; ≡SiOH), which is called the vicinal silanol group when it is bonded by an intramolecular hydrogen bond with other silanol group; and the geminal group (two hydroxyl

groups bonded to one silicon atom =Si(OH)$_2$) (Yang et al., 2006; Zhuravlev, 2000). The surface of silica can be activated using modification reactions with an organic compound to get new bonds, i.e. (≡Si–O–C≡, ≡Si–C≡, ≡Si–N=) through the reaction of the silanol functional group.

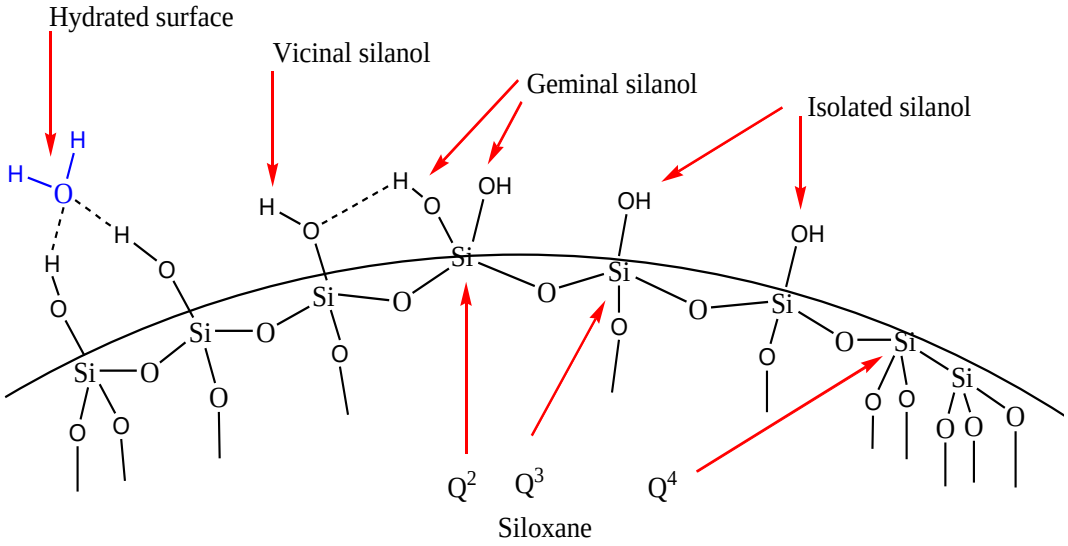

Figure 1.1: The various types of siloxanes and silanols in silica matrix.

1.3.3 Rice husk ash

Rice husk (RH), also called rice hull, is the hard outermost layer of rice seeds which protect the seed during the growing season. It forms on average 22% of the rice which is separated out during the husking process in the rice mills.

The world's paddy production in 2014 was 744.4 million metric tonnes of rice according to the rice market monitor, a report made by the Food and Agriculture Organization of the United Nations at October 2014 and, consequently, more than

150 million metric tonnes of rice husk which are mostly burnt outdoors or thrown on fallow land. Such cause disposal systems environmental problems. In many cases the rice husk are ignited resulting in poisons fumes. Since RH is highly resistant to moisture and fungus, it works as a good insulator (Mohanta et al., 2012).

Rice husk consists of 20% ash, 38% cellulose, 22% lignin, 18% pentose and 2% other organic trace compounds (Adam and Chua, 2004; Adam et al., 2006). Because of its large silica content (SiO_2), it rots slowly. When it is brought back to the fields, it causes poor food returns and, when burnt, the rice husk gives out 3,410 kcal/kg. Therefore, it represents a cheap source of renewable energy, but when used for energy generation, it gives about 17-26% ash, higher than the common fuels like wood 0.2-2% and coal 12.2% (Flörke, 2008).

The rice husk ash (RHA) contains 87-97% of amorphous silica (Della et al., 2002) and it has a variety of applications in material science, like being used in the production of Portland cement, supplying a very compact concrete, as an absorbent for oils and chemicals, a source of silicon, in the ceramics industry and as an insulation material (Flörke 2008).

A more specialized application is as a natural, perfect source of amorphous reactive silica, which is employed as an inorganic support for heterogeneous catalysts (Chumee et al., 2009). Figure 1.2 shows the conversion of yellow rice husk into white amorphous silica RHA.

Figure 1.2: The conversion of RH (a) to RHA (b, c) and their physical appearances. RHA (b) is a result of incomplete burning resulting black coloured char (Turmanova et al., 2011).

1.4 Mesoporous hybrid materials

Mesoporous organic-inorganic hybrid materials, a novel type of substance with large surface areas and a tunable pore size (Fujita et al., 2009), have been synthesised through the pairing of organic and inorganic constituents by using the template system. There are three ways to incorporate functionalities; sequent grafting of organic components onto the matrix of silica, one-pot condensation reaction of silica as an inorganic component with silylated compound as organic component and using bissilylated organic components to give periodic mesoporous organosilicas (PMOs) (Hoffmann et al., 2006).

1.4.1 Amorphous silica

In nature, silica is inert and it exists in amorphous and crystalline forms. The crystalline form comprises of a major portion of soil, sand and other various minerals like quartz, cristobalite and tridymite (Iler, 1979). Amorphous silica is an irregular form which is more highly hydrated than its crystalline form and is found as opal and infusible earth (Gregg and Sing, 1982). Silica exists in various amorphous forms called the dispersed system as described in Table 1.2.

1.4.2 Ordered mesoporous silica

The improvement of porous materials with high specific surface areas is actually an attractive research area, especially with respect to prospective applied fields such as gas stockpiling, sensor technology, adsorption, chromatography and catalysts. Since 1990, a big breakthrough in material synthesis took place when a Japanese group of researchers synthesized the first mesoporous nanoparticals of silica (Kato et al., 1990). Later, in 1992, the researchers of Mobil oil company developed periodic mesoporous silicate materials called Mobil Crystalline Materials (M41S) (Beck et al., 1992). These M41S materials subrogated zeolite molecular sieves which were held on a pore size about of 15Å; however, the M41S materials posses pore diameters of about 2−10 nm and manifest amorphous pore walls.

According to International Union of Pure and Applied Chemistry (IUPAC) classification, based on their pore size, microporous materials are classified as materials whose pore diameters are below 2 nm, while mesoporous materials are classified as materials whose pore diameters are in the range 2-50 nm and

macroporous materials are classified as materials whose pore diameters are above 50 nm.

Table 1.2: Amorphous dispersed systems.

Silica sol (colloidal)	It is an important type of amorphous silica, which can be prepared by sol-gel route (Brinker and Scherer, 1990) by polycondensation and polymerization reactions of a soluble silicate by adjusting the pH using an acid or base.
Silica hydrogel	It is rigid, coherent and includes three dimensional network, which can be prepared by proceeding of condensing reaction until the gelation point.
Silica xerogel	It is a partial collapsed gel, which can be made during the dehydration process of hydrogel and losing its pore filling liquid (mostly water).
Silica aerogel	It is a porous ultralight material with high pore volume, which can be prepared through supercritical drying process of a gel and replacing the liquid component with a gas.
Precipitated silica	It is dry silica with short distance characteristics structure (Parfitt and Sing, 1976). It occurs when the ultimate silica particles are coagulated as loose aggregates in the aqueous medium.
Pyrogenic silica (fumed)	It is anhydrous silica which is extremely low in bulk density and has a high surface area which can be synthesized by heating the silica at elevated temperatures (Otto et al., 2008).

The structures of M41S materials can be divided into: MCM-41 with a hexagonal arrangement of the mesopores; MCM-48 with a cubic arrangement of the mesopores; and MCM-50 with a lamellar structure (Figure 1.3) (Kresge et al., 1992).

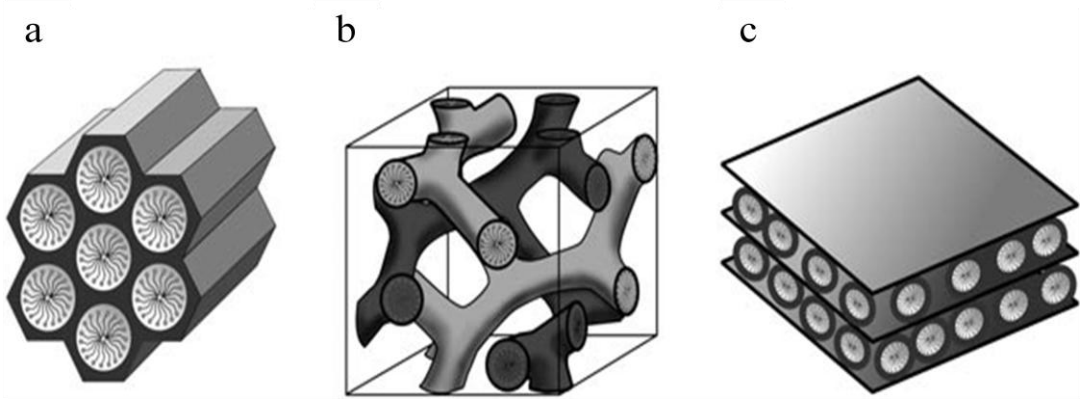

Figure 1.3: Structures of M41S materials: a) MCM-41 (2D hexagonal, *p6mm*), b) MCM-48 (cubic, *Ia3d*) and c) MCM-50 (lamellar, *p2*) (Kresge et al., 1992).

Eight years after the discovery of M41S materials, researchers from the University of California in Santa Barbara prepared silica nanoparticles which were called Santa Barbara Amorphous materials (SBA-15). These also involve a hexagonal mesoporous arrangement with large surface areas and pore volumes and act as excellent supports for several applications in chemistry (Zhao et al., 1998a).

1.4.3 Synthesis of ordered mesoporous silica

The synthesis of ordered mesoporous materials has been mentioned vastly in the literature. A suggestion of the steps for the synthesis of MCM-41 is shown in Figure 1.4. There are two routes: route (a) (true liquid-crystal templating procedure), which was proposed initialy by Mobil's researchers (Beck et al., 1992). The

synthesis of hexagonal silicate materials depends on the hydrophilic and hydrophobic properties of the molecules of the structure-directing agents, mostly long-chain alkyltrimethylammonium halides like cetyltrimethylammonium bromide (CTAB). When it is dissolved in water, its molecules will arrange themselves to form a micelle; the hydrophilic heads form the outside connect with the polar solvent (i.e. water) and the hydrophobic tails are directed inwards of the micelle because they are insoluble in polar solvents. These micelles will arrange themselves together to form a micellar rod. Sequentially over time, these new micellar rods will arrange to form a hexagonal array of micellar rods in solution. At the time of the preform process, when adding the silicate source like the tetramethylorthosilicate to the bulk solution, it will form a coating on the outside of the formed micelle rods. Route (b) follows another procedure suggested by Monnier et al. (1993), which is called cooperative liquid-crystal template mechanism. It implies that the silica and the structure-directing agents are first mixed, and then the surfaces of micelles in the silica environment are developed from sphere to rod and cluster-driven by non-covalent weak interactions like hydrogen bonding, van der Waals forces and electrostatic attraction (Zhao et al., 2012). After the process is completed, the obtained white product is filtered, washed, dried and the template molecules are removed by either calcination at 500 to 600 ^{o}C (Beck et al., 1992) or solvent extraction, i.e., by using ethanol, acid ethanolic solution or using the ion-exchange procedure (usually using NaCl or NH_4Cl) (Inagaki et al., 1999) to get the mesoporous material MCM-41.

The mesoporous material SBA-15 are synthesized by the same pathway, but the difference is that the SBA-15 is synthesized using non-polar surfactants like

polyethylene glycol as template agent in acidic conditions while MCM-41 is synthesized using CTAB in basic conditions (Zhao et al., 1998a, 1998b).

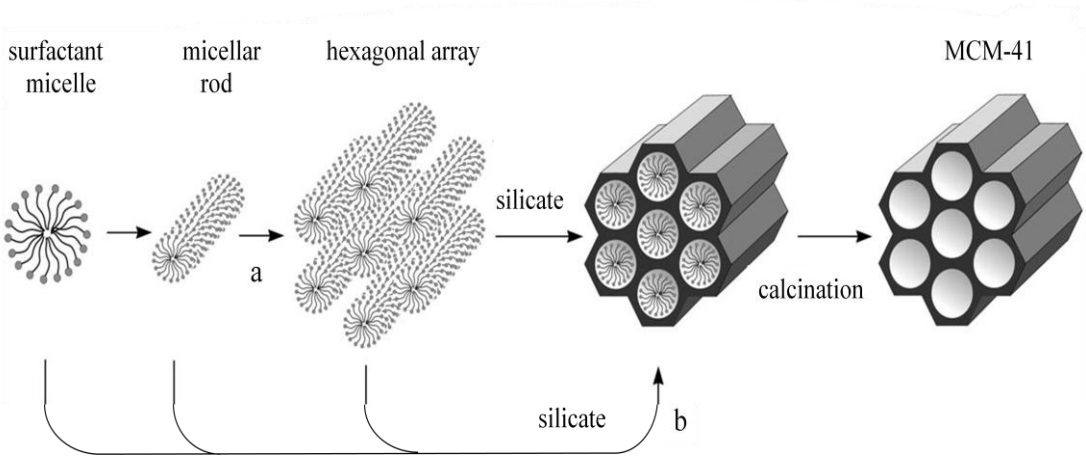

Figure 1.4: Probable pathways for the templated synthesis of ordered MCM-41 by structure-directing agents: a) true liquid-crystal template, b) cooperative liquid-crystal template mechanism (Monnier et al., 1993).

1.5 Organically functionalized mesoporous materials

The amalgamation of the properties of organic and inorganic construction units within a single material is a most interesting notion for scientists's estimation of materials. This would merge an enormous collection of organic functionality with the advantages of the inorganic substrate giving it robustness and thermal stability. The participation of organic and inorganic components can produce a united material whose properties vary comparatively from those of the solo, isolated components. This is particularly applicable to the heterogenization of the homogeneous catalysts when the inorganic materials can be modified with organic functionalities, like alcohols, thiols, amines, carboxylic and sulfonic acids, so that a real reaction can occur on a stable, hard inorganic matrix (Hoffmann et al., 2006).

Recently, more extensive studies have been developed to use hybrid organic-inorganic materials for different applications, such as optics, sensing, microelectronics, separation and catalysis.

In terms of the large pore size and high abundance of silanol groups on the surface of the mesoporous silica, this makes it a serious nominee for supporting different organic functions which can be located in the channels or in the pore walls. In this respect, there are three main approaches for the synthesis of porous hybrid materials depending on the organoalkoxysilane units (Figure 1.5);

1) Grafting approach; which is the subsequent amendments of the inner walls of the inorganic mesoporous silica.

2) Co-condensation approach (one-pot synthesis); which is a potential direct synthesis of mesoporous silica phase by the co-condensation of tetraalkoxysilanes [$(RO)_4Si$; i.e. Tetraethyl orthosilicate (TEOS) or Tetramethyl orthosilicate (TMOS)] with terminal trialkoxyorganosilanes of the type $(R\dot{O})_3SiR$ using a structure-directing agent (SDA).

3) Periodic mesoporous organosilica production approach; this was first used in 1999 (Inagaki et al., 1999; Melde et al., 1999) by hydrolysis and subsequent condensation reactions of the bridged organosilica precursors of the type $(R\dot{O})_3Si–R–Si(OR')_3$, which had long been known from sol-gel chemistry (Loy and Shea, 1995; Shea and Loy, 2001).

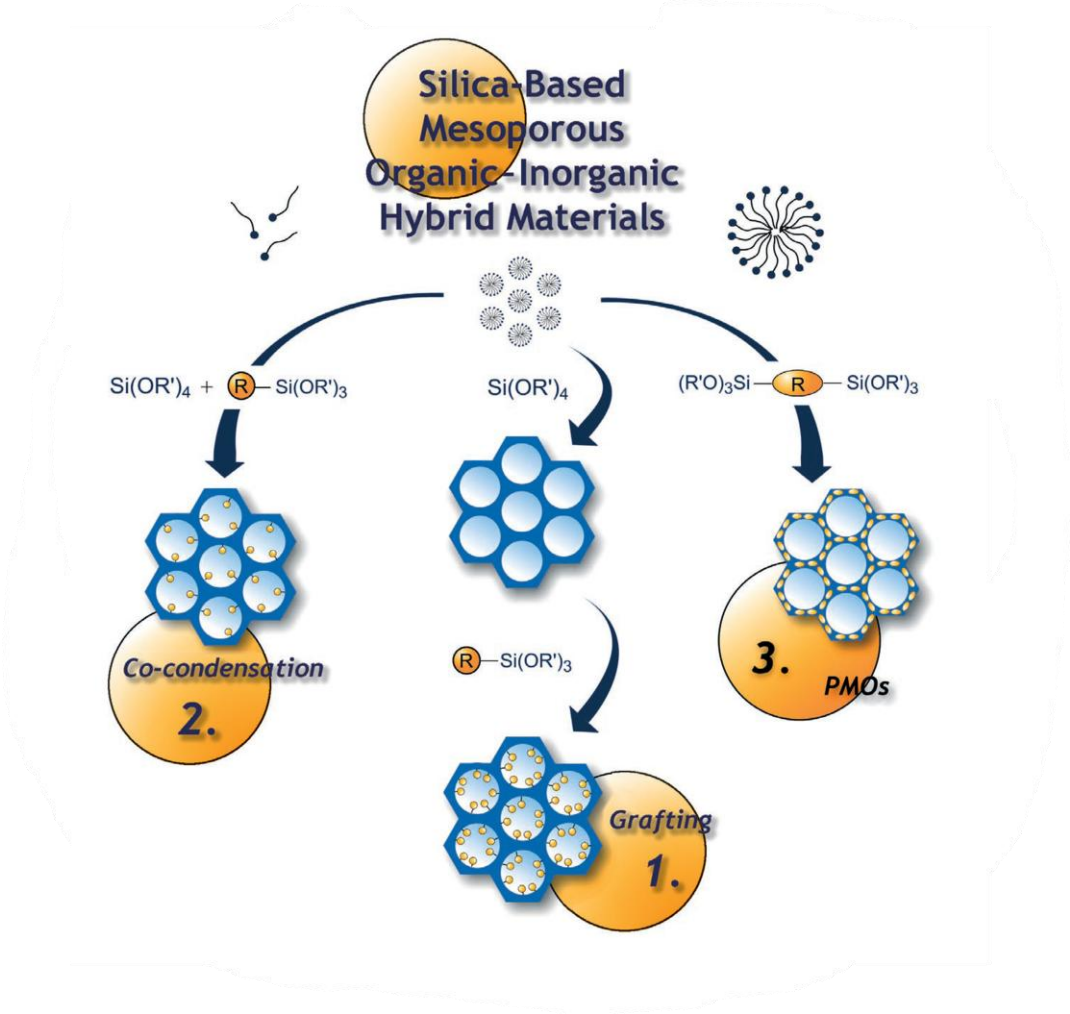

Figure 1.5: Three synthesis approaches for mesoporous hybrid materials (Hoffmann et al., 2006).

1.6 Metal incorporation in mesoporous materials

Metals incorporated in mesoporous materials have been widely reported for various numerous approaches inflation to catalytic applications. Many different metals have been inserted in the mesoporous materials, such as B, Al, Ga, In, Ti (Adam and Ahmed, 2008), and different transition metals, such as Mn, Fe, Co, Ni, Cu (Adam et al., 2013b; Sayari and Liu, 1997). The following sections will discuss two types of metal incorporation onto silica:

a) Incorporation of metal ions onto silica without organic ligands.

b) Incorporation of metal ions within organic ligands onto silica.

1.6.1 Incorporation of metals without organic ligands

1.6.1.1 Metal salts as metal precursors

The metals incorporated within mesoporous materials can be done by one-pot method or by post-treatment. In the one-pot method, metal salt is added from the beginning in the initial gel while the post-treatment can be carried out either by impregration or by ion-exchange; in both procedures the interaction occurs between the metal salt and the initially formed mesoporous silica. The resulting mesoporous materials resulting from one route is not necessarily similar to that of the other. The post-treatment also can be carried via grafting method. Tilley et al. (2002) synthesized single-site grafted catalysts using a technique called as precursor route. (^{i}PrO)Ti[OSi(^{t}Bu)$_3$]$_3$ and Ti[OSi(^{t}Bu)$_3$]$_4$ were used as precursor grafted onto MCM-41 and SBA-15, respectively (Fujdala, 2003; Nozaki et al., 2002). By utilizing this approach various mesoporous materials have been obtained with different single-site metal centers, such as Cr, Fe and V.

1.6.1.2 Metal complexes as metal precursors

In some cases, the right selection of the metal precursor in the post-treatment can produce a mesoporous material with high metal dispersion. (Bonneviot et al., 1990) have noticed that when $Ni(NH_3)_x(H_2O)_{(6-2x)}$ complexes are adsorbed on silica, they loose the aqua ligands through the replacement by $\equiv SiO^-$ from the silica surface. Moreover, the water molecules can easily replace the monodentate NH_3 ligands through drying and calcination process, forming nickel phyllosilicates and nickel hydroxide on the mesoporous material (Che et al., 1995). Using a bidentate

ligand such as ethylenediamine instead of NH_3 can produce more isolated metal species after calcination with high dispersion on the surface of silica (Sun et al., 2006).

1.6.2 Incorporation of metal ions within organic ligands

There are four identified methods for anchoring metal complexes onto mesoporous materials; i) encapsulation, ii) exchanging, iii) post-synthesis (grafting), and iv) one-pot synthesis. The first two methods are insignificant, with weak electrostatic interactions between the metal complex and the mesoporous support. Subsequently, the anchored complexes of these two methods are normally easily leached through the reaction process. The significant immobilization of complexes on solid support are usually accomplished by post-synthesis and one-pot synthesis methods by virtue of the formation of stable covalent bonds between a functional group (R′) and the solid support ≡Si-O-Si-R′.

1.6.2.1 Grafting incorporation (post-synthesis method)

There are numerous strategies for grafting metal complexes into the channel of mesoporous materials to create the active centers in the solid support. The activation of the mesoporous materials can be achieved efficiently due to their confinement effect and changeable of the hydrophilic-hydrophobic chemical environment compared to that of homogeneous complexes, which suffer deactivation due to their oligomerization probability. Herein, we are tallying the various grafting strategies to two kinds: direct grafting and indirect grafting.

1.6.2.1.1 Indirect grafting incorporation

The grafting of metal complexes can be established indirectly by grafting organic functional groups onto mesoporous materials such as numerous functioned propyltrialkoxysilanes to tethered organic moieties. A further modification can be done by a suitable nucleophilic substitution on the functionalized ligand leading to a metal complex through complexation with acertain transition metal. However, it is not possible to be certain whether all of the added metal salt reacts and is coordinated with the ligand or whether it is just physically adsorbed on the surface or pores of the support, so it can not be proven that the catalytic activity is facilitated due to the metal complex or the adsorbed free metal salt.

Herein, are selected examples from literature to illustrate this approach. In 2012, Sarmah et al. reported the indirect grafting of palladium(II) Schiff base complex onto silica (see Figure 1.6), where the Schiff base has been formed by the condensation between 3-aminopropyltriethoxysilane (APTES) functionalized silica gel and acetamide and then developed into a complex with palladium acetate (Sarmah et al., 2012). The materials obtained have been utilized for the Suzuki-Miyaura cross-coupling reactions of aryl halides. For the Suzuki-Miyaura reaction, the general catalyst used is $Pd(OAc)_2$. However this is a homogeneous catalyst which has all the disadvantages discussed earlier.

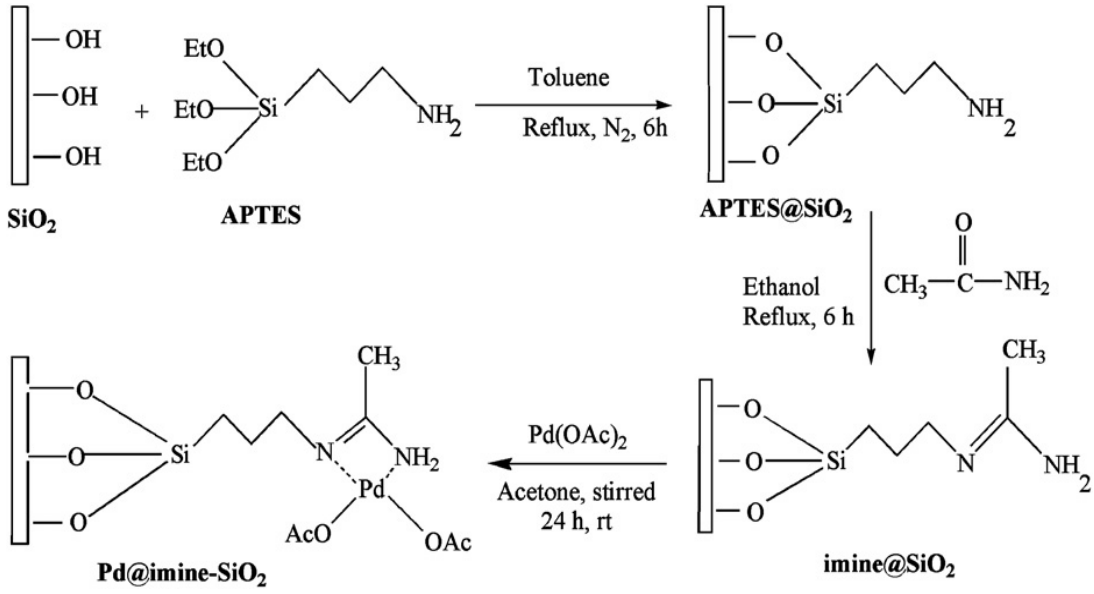

Figure 1.6: Indirect grafting of palladium(II) complex onto silica gel (Sarmah et al., 2012).

In 2011, Bhunia and Koner reported the preparation of nickel(II) Schiff base complex via post-synthesis method. The Schiff base obtained by the condensation of salicylaldehyde and 3-aminopropyltriethoxysilane (APTES), was anchored on MCM-41. The activity of the prepared catalyst was examined for epoxidation of olefins by using *tert*-butyl hydroperoxide as an oxidant (Bhunia and Koner, 2011) (Figure 1.7).

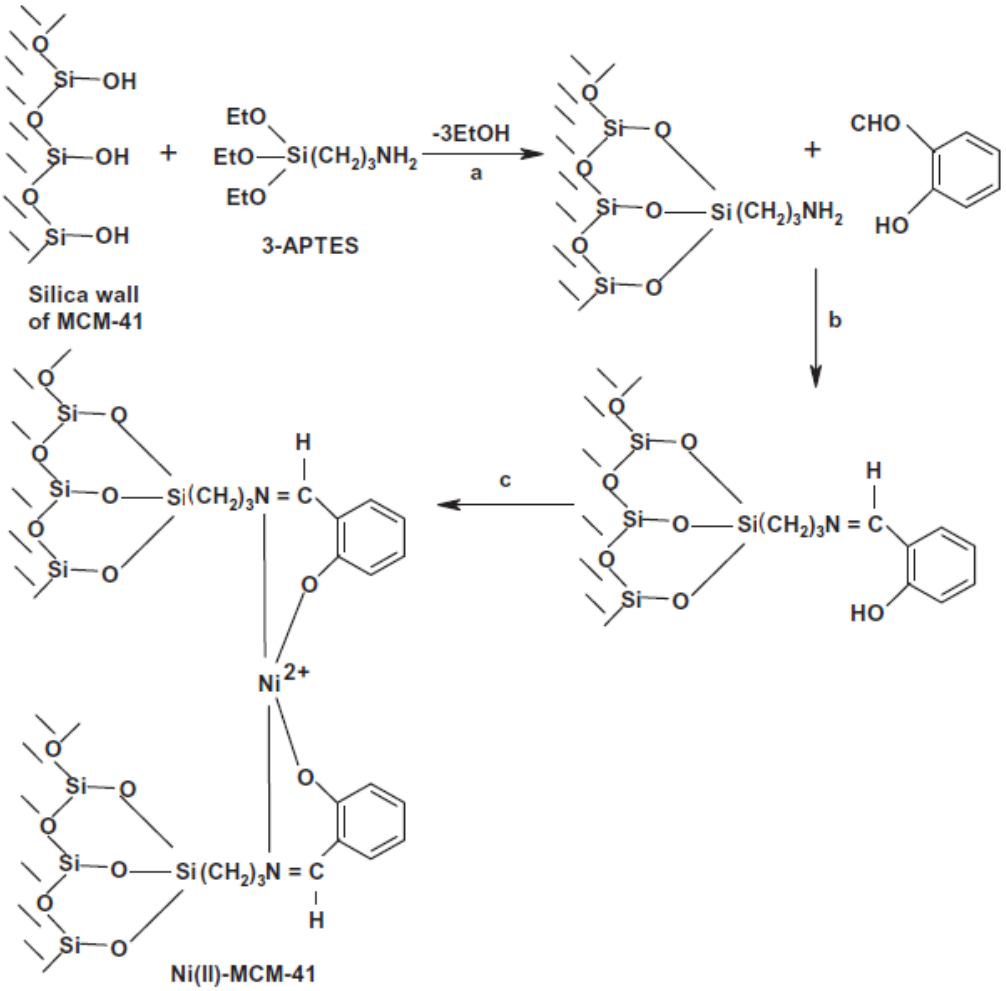

Figure 1.7: Indirect grafting of nickel(II) complex onto silica MCM-41 (a) functionalization, b) condensation, c) metal complexation) (Bhunia and Koner, 2011).

1.6.2.1.2 Direct grafting method

In the direct grafting, the metal complex is first produced at the molecular level, then it is immobilized as a whole onto the surface of mesoporous materials through a suitable organic silanes, whether it is inside the molecular construction of the metal complex or functioning on the surface of the mesoporous materials, as shown in the examples in Figure 1.8 and Figure 1.9 respectively.

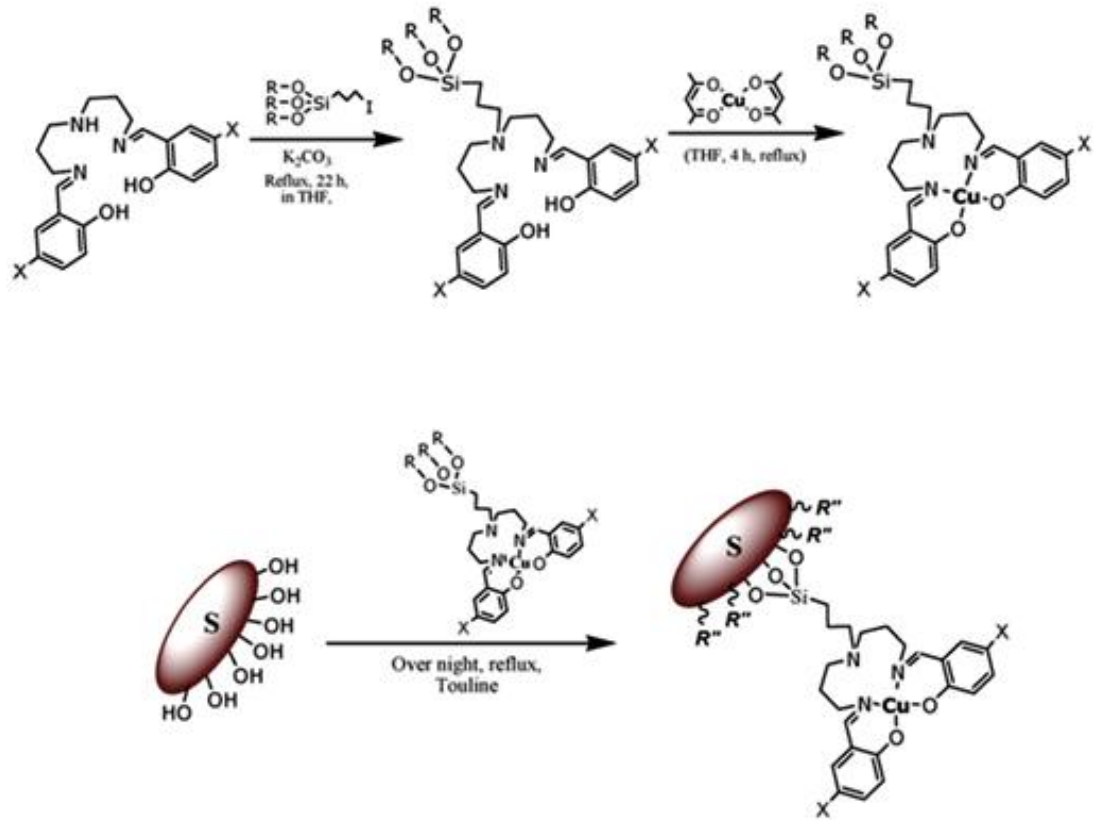

Figure 1.8: Synthesis of copper(II) complex covalently anchored on silica (s = silica) (Mishra et al., 2012).

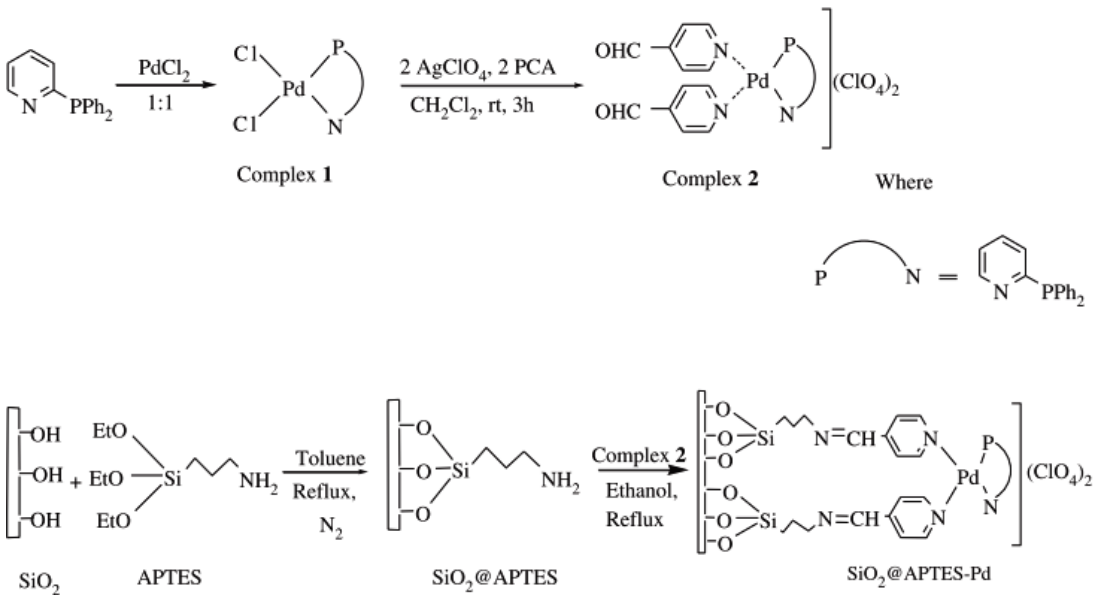

Figure 1.9: Immobilization of palladium complex onto silica gel through Schiff-base condensation (Sarmah et al., 2013).

1.6.2.2 One-pot incorporation

Successful mesoporous materials containing metal complex in their pore wall can be synthesized by co-condensation of a silica source such as common tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) and terminal trialkoxy organosilanes precursors with structure-directing agents (SDAs) by sol-gel chemistry. This is shown in Figure 1.10.

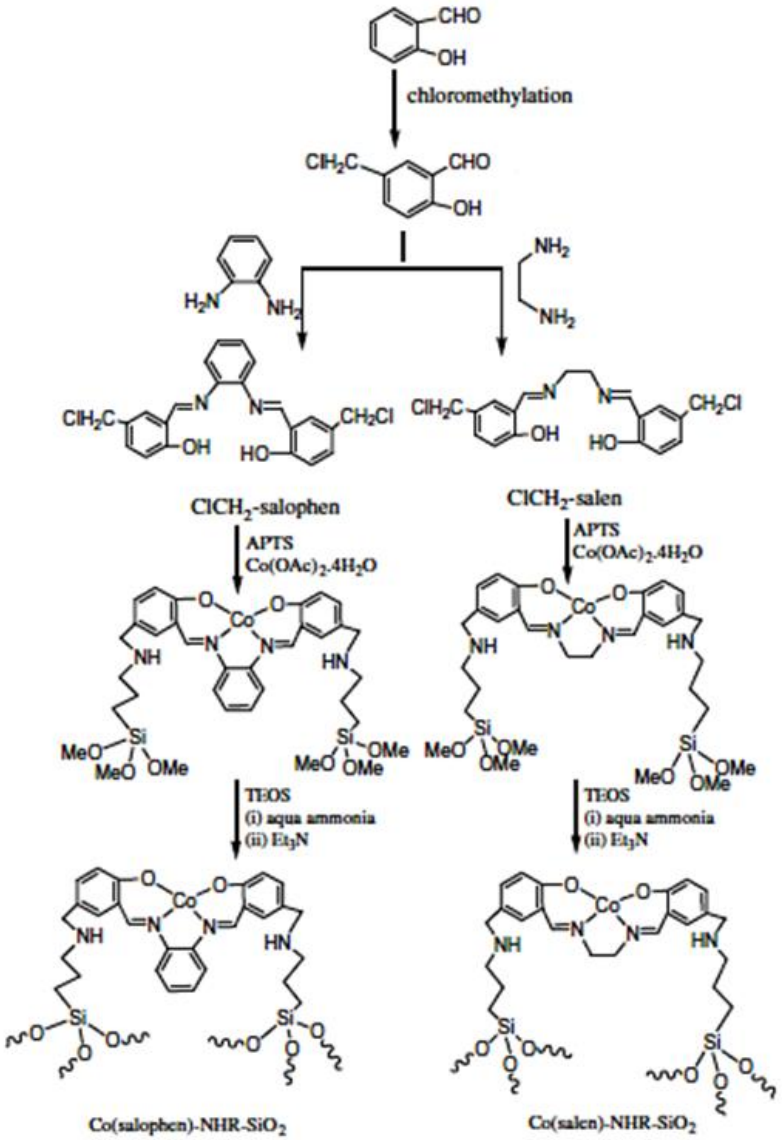

Figure 1.10: Preparation of immobilized catalysts via sol-gel process (Lijuan et al., 2009).

1.7 Salen Schiff base ligand and metal-salen complex

In 1864, the German scientist Hugo Schiff described the condensation of an aldehyde with an amine leading to the production of imine with general chemical formula $R_1R_2C=N-R_3$, known as the so-called Schiff base. A wide range of numerous types of Schiff base ligands can be coordinated with different metals through the imine nitrogen and another heteroatom, which can be oxygen, nitrogen or phosphine usually linked to the original aldehyde or ketone molecule to construct metal complexes (Cozzi, 2004).

The preparation of new metal complexes of Schiff bases is still interesting in catalyst chemistry. This is due to the ligands being easily prepared, supports substrate chirality, tuning the located metal, enhancing the solubility and stability. As a result, they were widely used in homogeneous and heterogeneous catalysts (Yoon and Jacobsen, 2003).

Salicyladimines (salens) are an example of Schiff base complexes which have been known since 1933 (Pfeiffer et al., 1933) and which can be formed by the condensation of salicyladehyde bearing different substituents with a primary 1,2-diamine (Figure 1.11). The salen complexes have been comprehensively studied, especially when Jacobsen (Jacobsen et al., 1990) and Katsuki (Katsuki et al., 1990) detected the enantioselective epoxidation of unfunctionalized alkenes by using catalysts of chiral Mn-salen complexes and went on to investigate various catalytic reactions by these types of complexes such as oxidation of hydrocarbons (Lee et al., 1998), aziridination of alkenes (Omura et al., 2004), Diels-Alder reaction (McGilvra and Rawal, 2004), hydrolytic kinetic resolution of epoxides (Shin et al., 2004), alkylation of aldehydes (Maeda et al., 2004) and oxidation of sulfides to sulfoxides

(Kim and Rajagopalba, 2003). In this work, the salen ligand was synthesized by condensation of 4-hdroxysalicyladehyde with 1,2-ethylenediamine and complexed with palladium and nickel ions.

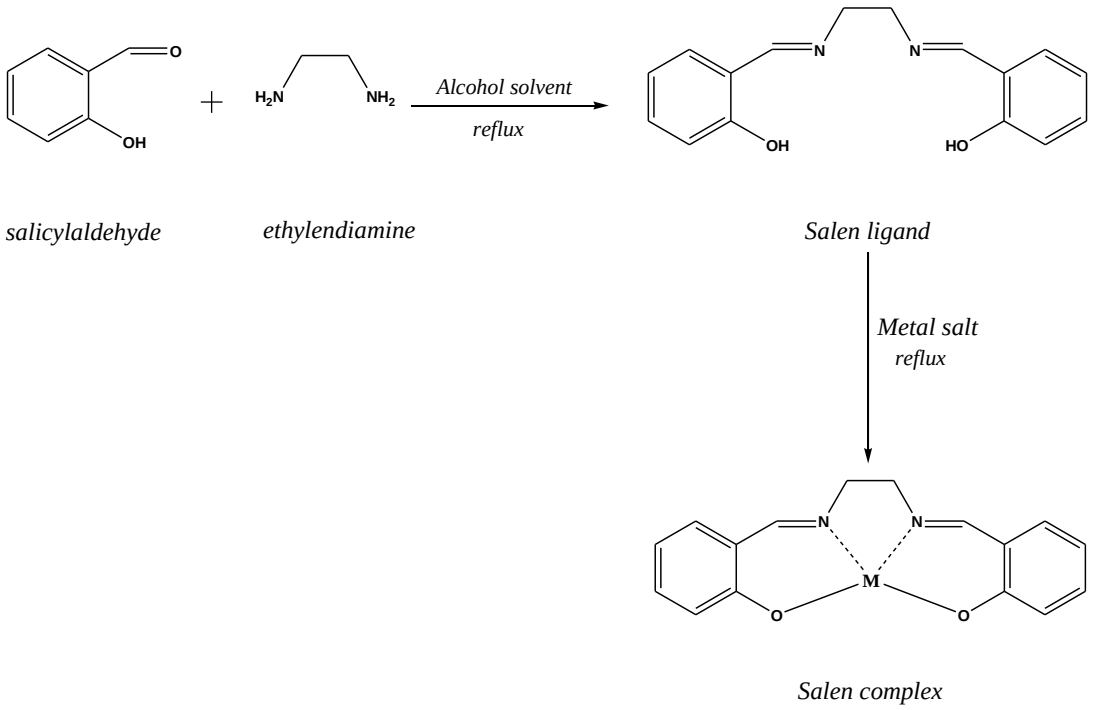

Figure 1.11: Synthesis of salen Schiff base ligand and salen complex (Jacobsen and Larrow, 1998).

1.7.1 Incorporation of metal-salen complexes onto mesoporous materials

The incorporation of metal-salen complexes onto mesoporous silica can be accomplished by grafting or by one-pot synthesis methods as referred to the above. In 2002, Baiker et al. was the first to immobilize the cobalt-salen and copper-salen complexes on xerogel and aerogel silica by sol-gel approach *via* co-condensation of *N*,*N*′-ethylenebis(salicylidenaminato) (salen) metal complexes with tetraethoxysilane under acid condition, with the complex possessing two imine bonds with metal

without any bridge connection for two nitrogen atoms. The material produced was used as catalyst for aerobic allylic oxidation of isophorone (Baiker et al., 2001; Murphy and Baiker, 2002) (Figure 1.12).

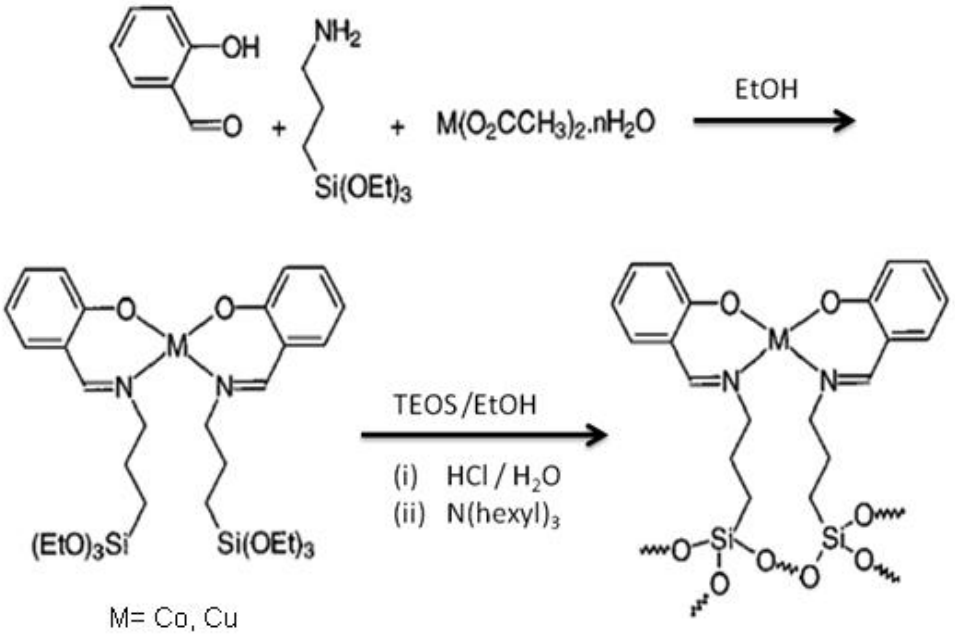

Figure 1.12: Sol-gel immobilization of Co-salen and Cu-salen complexes on silica gel (Baiker et al.2001).

Below are some reported examples for the incorporation of salen complexes formed by different linkages of the grafting or one-pot synthesis method.

In 2008, Zhang et al. synthesized the mesoporous silica-supported chiral Mn (salen) catalysts via the linking groups which are axially connected to Mn atoms via a linkage connected to the salen ligand. The prepared homogeneous and heterogeneous Jacobsen catalysts were evaluated in the asymmetric epoxidation of β-methylstyrene with NaClO as an oxidant (Zhang et al., 2008) (Figure 1.13).